Appendix A

Preparation of Pt thin films deposited by metalorganic chemical vapor deposition for ferroelectric thin films

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Abstract

Pure platinum films were deposited onto SiO_2(100 nm)/Si using $MeCpPtMe_3$ and oxygen by metalorganic chemical vapor deposition (MOCVD). Platinum deposition was controlled by gas phase mass transfer with an apparent activation energy of 2.2 kcal mol^{-1} within the temperature range of 300–450 °C. Film formation greatly depended on the nucleation and the growth rate according to the deposition temperatures. The deposition at 450 °C was mainly controlled by the growth rate and at 350 °C was governed by the nucleation rate. Holes formed on Pt films deposited at 350 °C were affected by the variation of oxygen flow rates. Holes within the films increased the film resistivity. MOCVD-Pt showed an excellent step coverage and a smooth and stable state after deposition of BST at 600 °C. © 1997 Elsevier Science S.A.

Keywords: Auger electron spectroscopy (AES); Chemical vapour deposition (CVD); Organometallic vapour deposition; Scanning electron microscopy

1. Introduction

Thin films of platinum are used extensively in microelectronics device processing [1,2], electrodeless metal plating [3], and protective coatings for specialized instruments [4]. Platinum is an excellent metal because of its low resistivity, high thermal stability, and corrosion resistance. Recently, Pt thin films have been used as bottom electrodes of semiconducting memory capacitors and they are mainly prepared by sputtering and ion beam deposition. When Pt films are deposited by sputtering, thin films have a large compressive stress and many pinholes are formed to relieve the compressive stress when ferroelectric thin films are deposited on the Pt bottom electrode at high temperatures (500–800 °C) [5]. Pinholes in ferroelectric thin films have a bad influence on the electrical properties of thin films. Therefore, when Pt films are prepared by CVD, compressive stress could be excluded [6]. Thermal deposition of platinum from the vapor phase has been reported with use of Pt(acetylacetonate)$_2$, Pt(PF$_3$)$_4$, or Pt(CO)$_2$Cl$_2$ [7,8]. These depositions require high temperature (200–600 °C), and the films are contaminated by heteroatoms from the ligands. Recently, many groups have reported chemical vapor deposition (CVD) using organometallic compounds [6]. In this study, Pt thin films were deposited using (methylcyclopentadienyl)trimethyl-platinum(MeCpPtMe$_3$), (CH$_3$)$_3$(CH$_3$C$_5$H$_4$)Pt, precursors

in the presence of oxygen by MOCVD. Kinetics of the film formation were mainly evaluated with the microstructure, and the possibility for a bottom electrode of the ferroelectric thin films was investigated.

2. Experimental procedure

Platinum films were deposited onto SiO_2(100 nm)/Si substrates by MOCVD. $MeCpPtMe_3$ as Pt precursor was used to grow the Pt thin films. Oxygen and hydrogen were used as reaction gases to deposit Pt films. The growth system used for the Pt deposition consists of a vertical cold-wall reactor and a gas flow system as shown in Fig. 1. The deposition was performed at the temperature range of 300–450 °C for the various deposition times. The Pt source was vaporized at 10 °C into a stream of 20 ml min^{-1} argon carrier gas. Both oxygen and hydrogen were introduced through a separate line at 10–50 ml min^{-1}. The detailed deposition conditions were tabulated in Table 1. The film thickness and the surface morphologies were determined from the cross-sectional and surface images by scanning electron microscopy (SEM, AKASHI DS-130C), respectively. X-ray diffraction (XRD, Rigaku D/MAX-RC) using CuKα radiation and Ni filter was used to determine the crystal phase and the preferred orientation of

137

the films. The film composition was determined by Auger electron spectroscopy (AES, Perkin-Elmer SAM 4300) and the film resistivity was measured with an electrometer using a four-point probe. Pt films were deposited on poly-Si patterning for the investigation of step coverage. $(Ba,Sr)TiO_3(BST)$ thin films were deposited onto MOCVD-Pt by plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD).

3. Experimental results and discussion

Fig. 2 shows Auger electron spectra of Pt thin films deposited at 450 °C using H_2 and O_2 reaction gases. Fig. 2(a) shows AES spectra of as-received and sputter-etched (for 0.6 min) Pt films deposited using hydrogen. Xue et al. [9] reported that platinum films grown from $MeCpPtMe_3$

Table 1
Deposition conditions of platinum films

Deposition parameter	Range
Deposition temperatures	300–450 °C
Substrates	SiO_2 (100 nm)/Si, Ta/SiO_2/Si, MgO (100)
Deposition time	80 s–12 min
Bubbling temperature of $MeCpPtMe_3$ [a]	10 °C
Ar gas flow rate of Pt source	20 ml min^{-1}
Oxygen and hydrogen gas flow rate	10–50 ml min^{-1}
Deposition pressure	2.0 Torr

[a] $MeCpPtMe_3$: (Methylcyclopentadienyl)trimethylplatinum: $(CH_3)_3(CH_3C_5H_4)Pt$.

in hydrogen were of exceptional purity. However, Pt films sputter-etched for 0.6 min contained a carbon (275 eV) as before. These results suggested that Pt deposition in hydro-
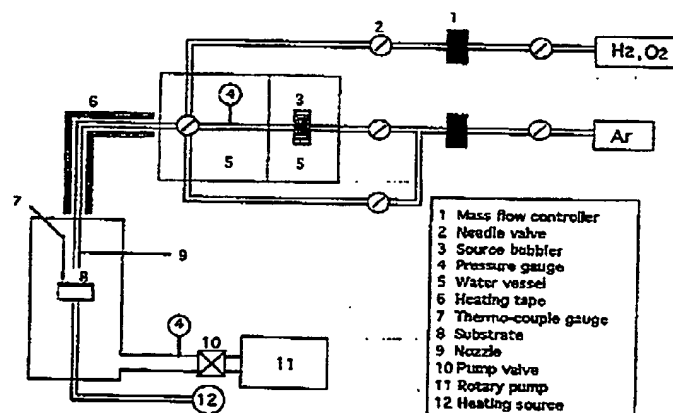

Fig. 1. Schematic diagram of the reactor for Pt chemical vapor deposition.
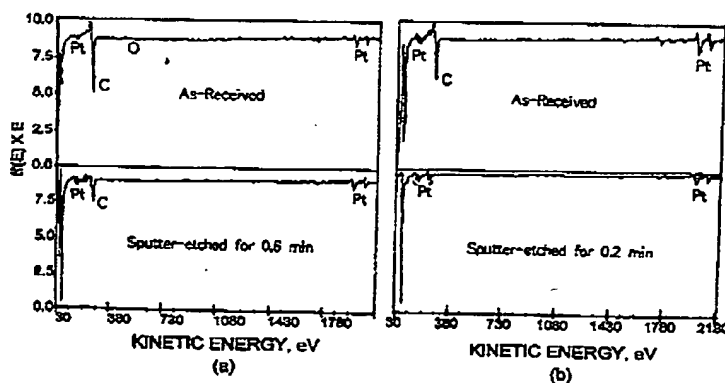
1 Mass flow controller
2 Needle valve
3 Source bubbler
4 Pressure gauge
5 Water vessel
6 Heating tape
7 Thermo-couple gauge
8 Substrate
9 Nozzle
10 Pump valve
11 Rotary pump
12 Heating source

Fig. 2. Auger electron spectra of Pt thin films deposited with (a) H_2 and (b) O_2 reaction gases (H_2 flow rate 60 ml min^{-1}, O_2 flow rate 50 ml min^{-1}).

138　　　　　　　　　　　J.-H. Kwon, S.-G. Yoon / Thin Solid Films 303 (1997) 136–142
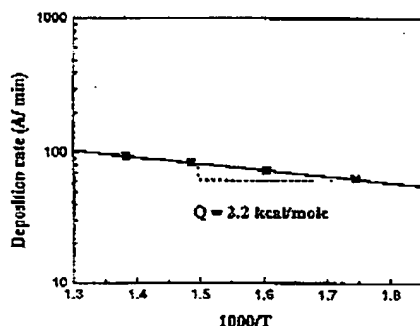

Fig. 3. The effect of the deposition temperature on the deposition rate.

gen was not enough to get rid of carbon contamination formed from the dissociation of MeCpPtMe₃. Auger electron spectra of Pt films deposited with oxygen instead of hydrogen are shown in Fig. 2(b). Although carbon is present on the surface of the as-grown film, the carbon peak disappeared after sputter-etching for 0.2 min and the

peak (241 eV) showing Pt only appeared. The carbon on the surface of the as-grown film is due to contamination caused by handling. The carbon originated from the dissociation of MeCpPtMe₃ reacted with oxygen at high deposition temperature and then products were exhausted from the reactor. Therefore, in this study, Pt deposition was performed using oxygen instead of hydrogen as the reaction gas.

Fig. 3 shows the effect of the deposition temperature on the deposition rate. As shown in Fig. 3, it is understood that the relation between deposition rate and $1/T$ consists of a straight line of small gradient under the present experimental conditions. In general, the deposition reaction is controlled by surface reaction when the apparent activation energy is between 10 and 50 kcal mol^{-1}, and by gas phase mass transfer when the apparent activation energy is less than 10 kcal mol^{-1} [10]. In Fig. 3, the apparent activation energy obtained by the least mean squares method is about 2.2 kcal mol^{-1}. Hence the deposition reaction was controlled by gas phase mass transfer in these experiments.
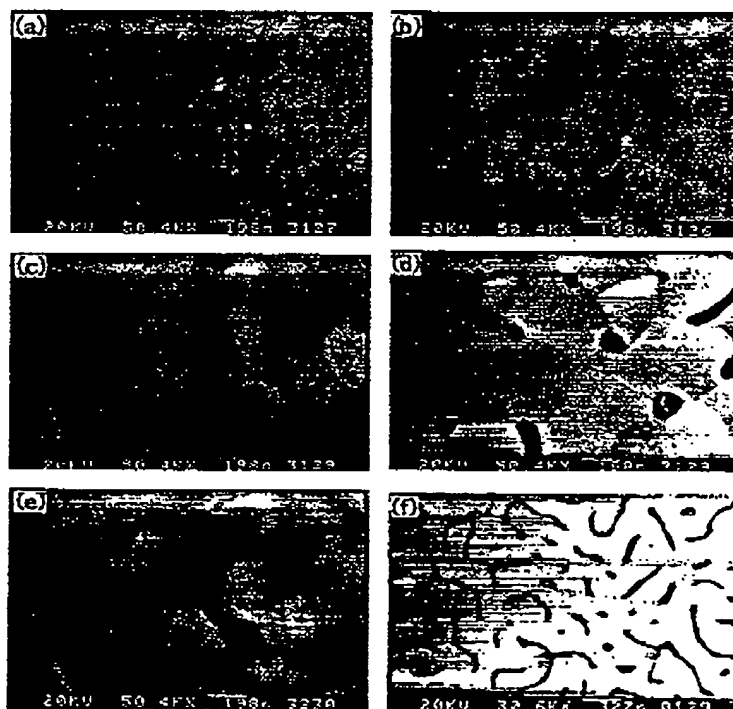
Fig. 4 shows SEM images of platinum deposited on

Fig. 4. SEM images of thin films deposited onto SiO₂/Si at various temperatures of (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) onto Ta/SiO₂/Si at 450 °C, and (f) onto MgO at 450 °C.
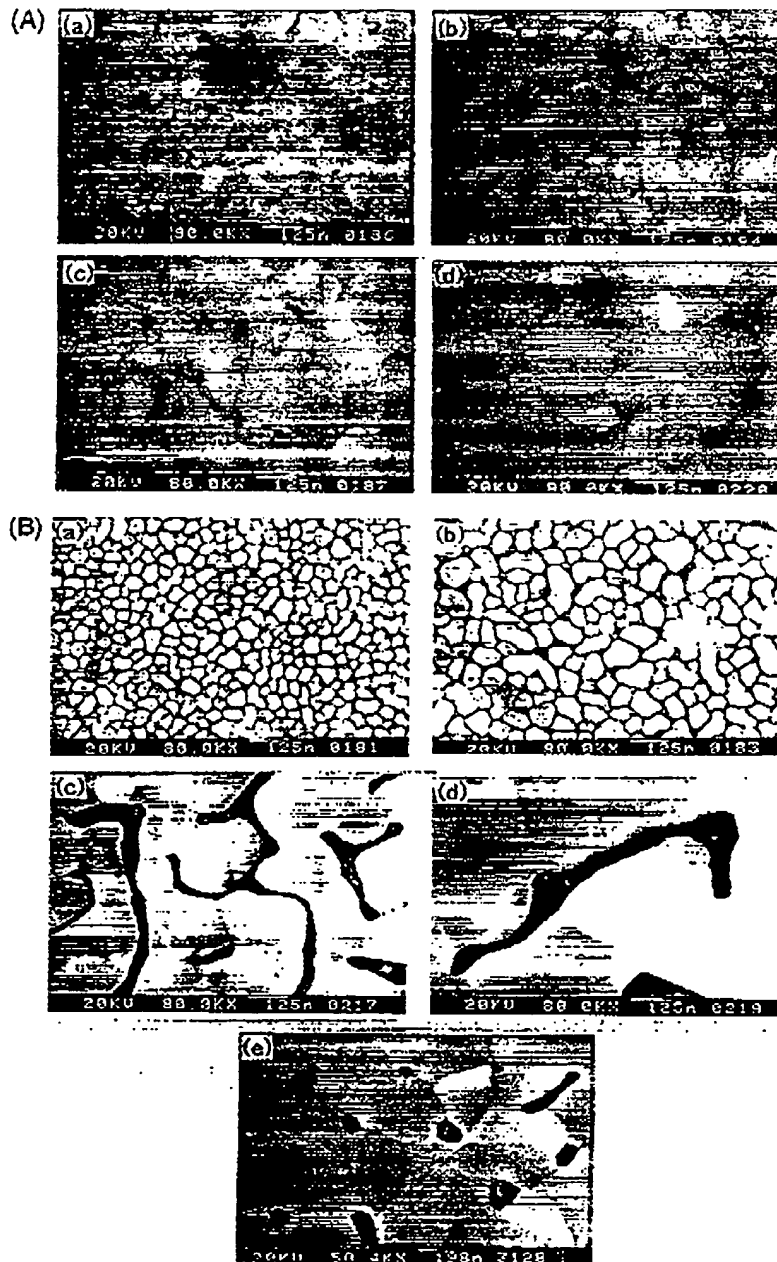
139

Fig. 5. SEM surface images of films deposited at (A) 350 °C and (B) 450 °C for various deposition times (deposition times of (A): (a) 80 s. (b) 2 min. (c) 3 min, (d) 6 min; deposition times of (B): (a) 80 s, (b) 3 min, (c) 6 min, (d) 9 min. (e) 12 min).
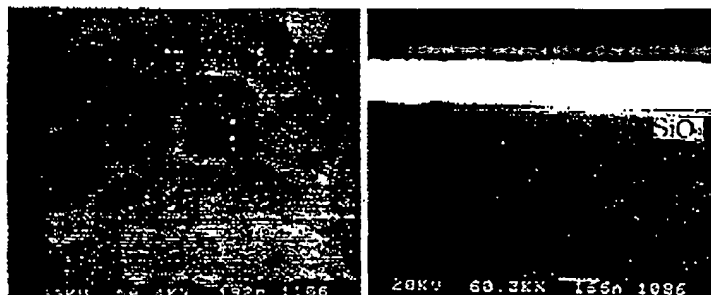
Fig. 6. SEM surface and cross-sectional images of Pt films deposited at 450 °C for 12 min (bubbling temperature of MeCpPtMe₃: 20 °C).

SiO₂/Si at various temperatures under the oxygen flow rate of 50 ml min⁻¹. Fig. 4(e) and (f) show the images deposited on Ta/SiO₂/Si and MgO substrates at 450 °C, respectively. The grain size of Pt films increased with increasing deposition temperatures. However, platinum films deposited at 400 °C show a few holes and at 450 °C show many holes at grain edges. The formation of holes at 450 °C could be explained as follows: the first reason is the formation of a second phase such as Pt₃Si, possibly by a reaction with Si substrate at high deposition temperatures; the second is the relationship of the nucleation and the growth rate with the deposition temperatures. The first reason can be examined through the surface morphologies as shown in Fig. 4(e) and (f). If many holes were the second phase formed by reaction with Si substrate at 450 °C, platinum films deposited on Ta/SiO₂/Si and MgO substrates should not show any holes. However, films deposited onto MgO substrate at 450°C also show the same holes as those of Si substrate. Therefore, the formation of holes at high temperatures (450 °C) should be explained differently. The second reason can be examined through the microstructure shown in Fig. 5. Fig. 5(A) and (B) show the SEM surface images of films deposited at 350 °C and 450 °C, respectively, for various deposition times. Oxygen flow rate during the deposition was kept at 50 ml min⁻¹. Films deposited for 80 s at 450 °C already had a mean grain size of about 40 nm and had many crevices between the grains. However, films deposited for 80 s at 350 °C contained more grains than those at 450 °C and only a few and small crevices. Films deposited for 3, 6, 9 and 12 min at 450 °C showed an abrupt grain growth and large holes with increasing deposition times. Although the films were deposited over long times, holes did not disappear any more. However, the crevices of the films deposited at 350 °C decreased as the deposition time increased and eventually films deposited for 6 min showed a smooth microstructure without any holes. Films deposited for longer than 6 min showed an almost similar structure to those of 6 min. The nucleation and the growth rate were greatly dependent on the deposition temperature. The deposition at 350 °C suggested that the nucleation rate

was dominant compared with the growth rate. Therefore, platinum film was almost completely covered with the grains at the initial stage of deposition. From the microstructure of films deposited at 450 °C, we can conclude that the deposition at 450 °C was governed by the growth rate rather than the nucleation rate and the deposition at 450 °C was not enough to get rid of holes. Fig. 6 shows the SEM surface and cross-sectional images of Pt films deposited at 450 °C for 12 min. The bubbling temperature of the Pt source was about 20 °C. The concentration of MeCpPtMe₃ was about two times as large as that of Fig. 5(b)–(e). The increase of Pt source concentration increases the thickness of Pt films from 150 to 220 nm and decreases the hole size of Pt films. As mentioned in relation to Fig. 3, these experimental results suggested that the Pt CVD was controlled by the gas phase diffusion mechanism.

Fig. 7 shows the variation of film resistivity for various oxygen flow rates. Fig. 7 also reveals the influence of holes on the film resistivity. Resistivity of films deposited at 350 and 450 °C monotonically decreased with increasing oxygen flow rates. The solid line indicates the bulk resistivity of platinum. The resistivity of films deposited at
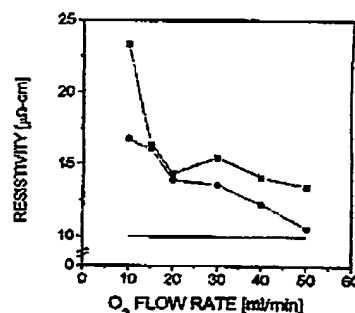

Fig. 7. Dependence of the film resistivity on oxygen flow rates. (–■–: deposition temperature 450 °C ; –●– : deposition temperature 350 °C ; ———: bulk resistivity of platinum).

450 °C was almost the same as that at 350 °C up to 20 ml min⁻¹ of oxygen flow rate, but increased by a factor of about 1.3 when the oxygen flow rate increased from 20 to 50 ml min⁻¹. The reason for these results could be explained with the microstructures of Pt films deposited with various oxygen flow rates at 450 and 350 °C as shown in Fig. 8(A) and (B), respectively. As shown in Fig. 3, because platinum deposition was controlled by gas phase mass transfer, film formation was affected by the concen-

tration of MeCpPtMe₃ and oxygen. However, the concentration of MeCpPtMe₃ was always constant in this experiment regardless of the variation of oxygen flow rate. As shown in Fig. 8(A), platinum films deposited at 450 °C have many holes in spite of the increase of oxygen flow rates because the film formation was controlled by the growth rate. However, because films deposited at 350 °C (Fig. 8(B)) were governed by the nucleation rate, the many small holes formed at small oxygen content decreased with
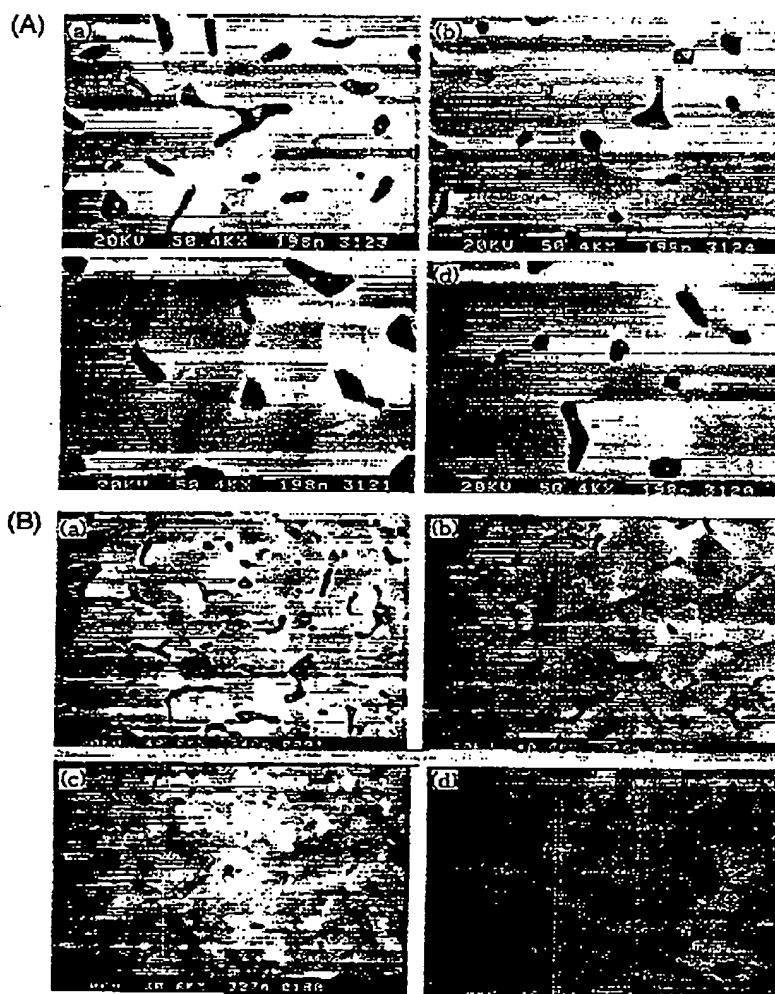

Fig. 8. SEM surface images of Pt thin films deposited at (A) 450 °C and (B) 350 °C for various oxygen flow rates (Oxygen flow rates of (A): (a) 10, (b) 20, (c) 30, (d) 40 ml min⁻¹; Oxygen flow rates of (B): (a) 10, (b) 20, (c) 30, (d) 40 ml min⁻¹).
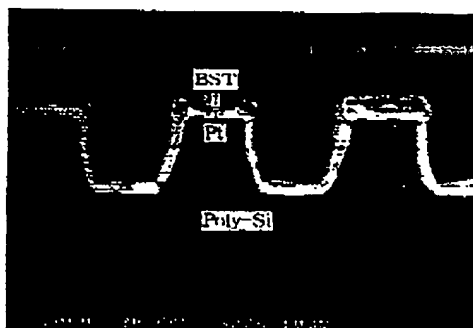
Fig. 9. SEM photograph indicating Pt step coverage on poly-Si patterns. (Deposition temperature of Pt: 350 °C).

increasing oxygen content and completely disappeared at the oxygen flow rate of 40 ml min^{-1}. Films deposited at 350 °C had many holes up to the oxygen flow rate of 20 ml min^{-1} and holes abruptly decreased on increasing above 20 ml min^{-1}. Therefore, resistivities of films deposited at 450 and 350 °C for the variation of oxygen flow rates were greatly dependent on the holes in films.

Fig. 9 shows a SEM photograph indicating the Pt step coverage on poly-Si patterns. (Ba,Sr)TiO$_3$(BST) films were deposited on Pt film at 600 °C by plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD). MOCVD-Pt showed an excellent step coverage and a smooth and stable state after deposition of BST at high temperature. However, PEMOCVD-BST film showed a poor step coverage.

4. Conclusions

Platinum films by MOCVD were controlled by gas phase mass transfer in these experiments. The growth mechanism revealed that the deposition at 450 °C was governed by the growth rate and at 350 °C was controlled by the nucleation rate. Holes formed at the grain edges greatly affected the film resistivity. Platinum films deposited at 350 °C and oxygen flow rate of 50 ml min^{-1} did not show any holes and showed almost similar resistivity (10.5 μΩ cm) to that of the bulk. The platinum bottom electrode showed excellent step coverage and a stable and uniform state after deposition of (Ba,Sr)TiO$_3$ thin films at 600 °C by plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD).

Acknowledgements

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